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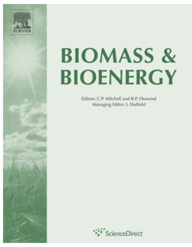

Mechanical and compositional characteristics of steam-treated Douglas fir (*Pseudotsuga menziesii L.*) during pelletization

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ABSTRACT

Rheological properties of pelletizing steam-treated Douglas fir at four different severities were investigated. Steam-treated wood pellets exhibited three compression regions that became more distinct with increasing treatment severity. Hydrolysis of hemicelluloses and condensations of lignin led to an increase in elasticity of pellets made from steam treated feedstock. The increased treatment duration improved the dimensional stability of pellets. The increase in particle surface roughness and concentration of mono-sugars and extractives contributed to the increase in required energy for extruding steam treated pellets from the die. The maximum breaking force, Meyer hardness and the hardness modulus increased with steam treatment. The increased hardness and dimensional stability of steam-treated pellets can be attributed to the binding role of mono-sugars released from Douglas fir during steam treatment.

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1. Introduction

Wood pellets are made from compacting logging and mill wastes. With a specific gravity of 1.1, slightly more than water, wood pellets can be handled similar to grains. In 2013 the Canadian wood pellet production capacity is about 1.8 Mt, roughly 15% of the global 12 Mt production. The global market is predicted to double and even triple the annual production by 2020. Most Canadian pellets are sold to Europe as a coal substitute for electric power generation, meanwhile new markets are emerging in Pacific Rim countries (e.g.: Japan and South Korea). In Canada, Ontario has initiated converting Atikokan coal thermal generating station to burn the biomass pellets. More domestic markets are evolving in the Canadian prairies. The Wood Pellet Association of Canada (WPAC) reports more than 40 producing plants in Canada and more than 50 associated industries that support wood pellet production, handling and shipping. Wood pellets are hygroscopic and tend to lose their integrity during handling and storage. Efforts are underway to treat biomass thermally or hydrothermally to improve

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its hydrophobicity. The new so called torrefied pellets have a larger calorific value than regular pellets. The hydrophobicity and increased calorific value allow the utilities considering co-firing biomass with coal to minimize their investments in logistics and modifications in combustion technology.

Torrefaction can be achieved through two processes, dry torrefaction [1] and wet torrefaction [2–4]. In dry torrefaction, the biomass is heat treated in an oxygen free environment with nitrogen. In wet torrefaction, the biomass is treated either in hot water or in a steam chamber. It has become evident that dry torrefaction of a biomass destroys its natural binding capacity to make durable pellets. For example, a previous group of researchers reported that no pellets can be produced from sawdust treated at 300 °C with the die temperature of 90 °C [1,5]. Some pellets that were formed at a lower temperature of 275 °C were defective. They reported some pellets could be made at elevated die temperature of 170 °C [5]. In contrast to dry torrefaction, hydrothermal treatment using steam was reported to be an effective pretreatment to make pellets made from woody biomass [2–4]. Steam treatment improved the mechanical strength and moisture adsorption resistance of pellets. Pellets made from steam exploded wood had a breaking strength 1.4–3.3 times than the strength of the pellet made from untreated wood with the same pelletization condition [2,6]. It was postulated that a modified restructure of lignin after steam explosion contributes to the increase in breaking strength. The effect of hydrothermal carbonization on pellets made from loblolly pine treated in inert high pressurized water with temperatures ranging between 200 and 260 °C for 5 min to several hours were studied [4]. Most of the reaction seems to occur within the first 20 min of the treatment.

A few researches have reported the pelletizing properties of untreated woody biomass using a single die system [7,8] and the effect of pelletizing conditions on the wood pellet quality using a pilot scale pellet mill [9–11]. The correlation between single die and commercial pellet mill and developing a process model was attempted with some degree of success [12]. A constitutive model of densification of agricultural biomass was studied to explain the pelletizing process [13]. The developed pelletization models required inputs of material characteristics (e.g. elastic and hardness moduli of particles in bulk, Poisson ratio, etc.). A more relevant mechanical property is the asymptotic modulus, which is defined as the ability of a compressed powder to sustain a compressive stress [14–16]. Researchers have applied asymptotic modulus to compare the compression behavior of different types of agricultural biomass. For example, it was found that decreasing the particle size and moisture content of cereal straw significantly increased the asymptotic modulus values of the resulted pellets [15].

The objective of the research presented here is to perform a detailed mechanical analysis of pelletization of steam-treated Douglas fir, based on force – displacement and/or stress–strain diagrams. Stress relaxation analysis is carried out to explore possible relationships between chemical and rheological properties of bulk wood particles under compressive stresses and their effect on dimensional stability of the steam-treated pellets. The detailed analysis elucidates the binding role of sugars and lignin quantitatively. The measured parameters will be useful for improving the pelletization process to produce durable pellets from a thermally treated feedstock.

2. Materials and methods

2.1. *Materials*

Douglas fir *(Pseudotsuga menziesii L.)* wood chips were collected from piles of wood chips at Fiberco facilities in North Vancouver, B.C., Canada. The wood chips were made from disc chipping of debarked trunk of Douglas fir trees grown in British Columbia, Canada. The full history of these chips is unknown but generally the wood chips that were made in interior BC were immediately transported to Fibreco by train. The wood chips were piled in the yard and remained there not more than a month. For loading, the chips were pushed to a long belt conveyor to be conveyed to barges or ocean vessels. The chips are destined for pulp and paper plants along Canada west coast or overseas operations (e.g. Japan).

2.2. *Sample preparation*

Once in the laboratory, the wood chips were processed as outlined in Fig. 1. The details of each unit operations are outlined in the following sections.

2.2.1. *Drying and size reduction*

Sampled wood chips had a moisture content of approximately 55% mass fraction (moisture contents are expressed in wet mass basis otherwise stated) according to ASABE standards [17]. To prepare samples for tests, the wood chips were initially dried to a water mass fraction of 25% in an oven at 103 °C. Dried samples were size reduced in a hammer mill using a screen openings of 1.6 mm. Ground wood was further dried at 50 °C in the oven to a water mass fraction of 10%. The dried ground particles were stored in sealed plastic bags placed in refrigerator at 4 °C until testing.

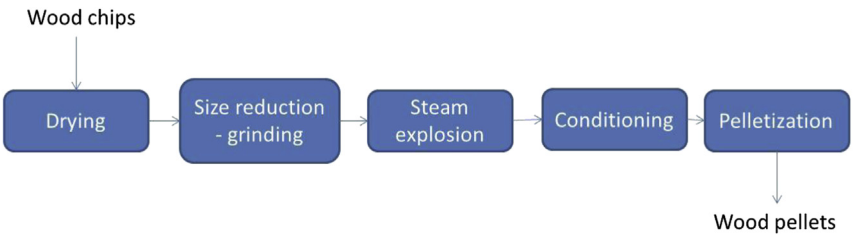

Fig. 1 – Schematic diagram of the experimental procedures of steam treatment and pelletization.

2.2.2. Steam treatment

The batches of ground wood were first conditioned to room temperature by removing the sealed sample bags from refrigerator and placing them on the laboratory's work bench for 24 h. A batch of about 50 g ground sample was heat treated in a 1 L high pressure steam chamber at a temperature of 200 and 220 °C (corresponding pressure of 1.6 and 2.4 MPa) [2] for 5 min. Upon completion of the treatment, the steam chamber was decompressed and the treated ground biomass was released into a chamber open to atmospheric air. The wet treated biomass was collected and placed in sealed plastic bags stored at 4 °C. The moisture content of a subsample was measured using the ASABE method [17]. Inpreparation for pelletization, batches of the treated samples with the moisture content between 10%–30% were dried in a convection oven set at 50 °C. Each batch was removed from the oven when the average moisture content of the biomass was about 10%. The dried samples were stored in sealed plastic containers stored at 4 °C until pelletization.

2.3. Particle size distribution

The size distribution of both treated and untreated ground samples was determined according to the ASABE standard S319.3 [18]. Prior to sieving analysis, samples were conditioned to 10% moisture content (w.b.). Roughly 20 g of a ground biomass was placed on top of a stack of sieves on a Ro-Tap shaker (Tyler Industrial Products, OH USA). Sieve mesh numbers used were 18, 25, 35, 45, 60, 80, 100, 120, 170 and 230 corresponding to nominal sieve openings of 1, 0.707, 0.500, 0.354, 0.250, 0.177, 0.149, 0.125, 0.088 and 0.063 mm. The mass retained on each sieve was weighed on an electronic balance to 10 mg precision. The geometric mean diameter (d_{gm}) of particle diameter was calculated according to the ASABE Standard S319.4 [18]. The sieving test was repeated three times for each sample.

2.4. Pelletization

Single pellets were made in a piston-cylinder electrically heated pellet making device. The design and operation of the pellet device have published previously [2,6]. Inpreparation for making a pellet, the electric power to the heater was turned on to heat the body of the cylinder to 70 °C. A temperature controller maintained the preset temperature. The cavity with 6.4 mm diameter in the cylinder was filled with approximately 500–800 mg of ground biomass using a spatula. The biomass rested on a cylindrical plug about 10 mm long and 6.2 mm diameter (the same diameter of the pressing piston) fitted in the cavity. The plug rested on a removable platform.

The bulk biomass in the cylinder was compressed by forcing down the piston rod at 6.67 mm min^{-1} to the maximum preset force of 4000 N (i.e., compaction pressure: 130 MPa). The piston was held at this pressure for 30 s for stress relaxation. The removable block was removed from the underneath of the plug. The cross head was activated to move downward at a speed of 13.34 mm min^{-1}. The piston pushed the formed pellet and the spacer out of the bottom of the cylinder.

The force–displacement data were logged during the entire cycle of compression and expulsion. The elastic modulus of the compacted samples was determined from the initial slope of each curve before the strain of 0.01% from the stress–strain graph [19]. The energy consumption of pellet compression and extrusion were calculated by the integration of the area under the force–displacement curve. The pellet was cooled to room temperature and stored inside a sealed glass bottle for further measurements. At least 15 pellets were made from each steam treated and untreated wood sample.

2.5. Stress relaxation and hardness test

The relaxation data for each sample were analyzed by the method described in Refs. [14,20]. The force vs. time curve during relaxation was normalized and linearized and represented as a straight line,

$$\frac{\sigma_0 t}{\sigma_0 - \sigma(t)} = k_1 + k_2 t \tag{1}$$

where σ_0 is the initial stress (MPa), $\sigma(t)$ the stress after time t at relaxation (MPa), t is time (s) and k_1, k_2 are constants.

The visco-elastic slope, k_2, can be used to quantify the degree of plastic flow under compaction [21]. Materials with a high visco-elastic slope value, k_2, exhibit a greater degree of plastic flow under compression. This parameter was found to correlate well with forming strong tablets at low compaction temperatures [21]. The slope k_2 of the straight line must be greater than one, and from a rheological point of view, the slope can be considered as an index of how solid the compacted specimen is on a short time scale. Any large value of greater than one is an indication of the existence of stresses that remain unrelaxed [16]. The residual stress can also be defined as the percentage (%) of the stress at relaxation time (t) over the initial stress.

The asymptotic modulus (E_A) is an empirical index of solidity that is the ability of the compressed powder to sustain unrelaxed stresses [16]. Equation (2) can be derived from the equation (1) as shown in the Appendix. E_A is defined as

$$E_A = \frac{\sigma_0}{\varepsilon}\left(1 - \frac{1}{k_2}\right) \tag{2}$$

where E_A is the asymptotic modulus (MPa) and ε is the strain (dimensionless or m m^{-1}).

Equation (1) is fitted to the stress relaxation data to estimate k_1 and k_2. The estimated k_2 value is then used in Equation (2) to calculate E_A.

In this research, a single pellet was placed between two anvils of the MTI system to measure the breakage. Details and the picture of the setup were described in the previous work [2]. The compression was diametrical. The hardness modulus of the pellet was determined from the initial slope of each curve before the strain of 0.01% from the stress–strain graph and expressed in GPa. The maximum load to break a pellet was recorded. The Meyer hardness (H_M) is defined as the applied force divided by the projected indentation area [2],

$$H_M = \frac{F}{\pi(Dh - h^2)} \tag{3}$$

where H_M is the Meyer hardness (N mm^{-2}), h is the indentation depth (mm), D is the initial diameter of a pellet cross section (mm^2), and F is the maximum force when the pellet is crushed (N).

2.6. Physical characterization

The mass, length and diameter of each pellet were measured immediately after its removal from the cylinder to calculate initial pellet density. These measurements were repeated after storing the pellets inside a sealed glass bottle for one week. A specific density was determined by measuring the total pore volume in a pellet by compressing nitrogen at 0.1 MPa into void spaces of the pellets using a Quantachrome Multipycnometer (Quantachrome, Boyton Beach, FL, USA). The weight of the pellet was measured using an electronic balance to 10 mg precision.

Moisture contents of the samples before and after pelletization were analyzed according to ASABE standard S358.2 [17]. Roughly 1 g of either ground sawdust or a whole pellet was used for moisture content measurement. Triplicate samples were oven dried at 103 °C for 24 h. The ash content was determined in triplicate as the mass fraction of residue remaining after dry oxidation at 550–600 °C [22]. Ash content analysis was made in three replicates. The high heating value of the pellets was determined by the oxygen bomb calorimeter (Parr 6100) from two replicates. Elemental analysis was performed on measuring the percentage of Carbon (C), Hydrogen (H) and Oxygen (O) of the untreated and steam treated samples by an elemental analyzer (Carlo Erba, EA 1108, Italy).

2.7. Chemical characterization

Prior to composition characterization, the steam exploded particles were further ground in a Wiley Mill with 40 mesh screen to prepare suitable particle size for Klason lignin determination. The ground particles were bone dried at 105 °C until no weight reduction was observed. Extractive contents were analyzed using TAPPI modified acetone extraction method (TAPPI-T-280 pm-99, 1999) [23].

The water soluble (WS) fraction of hydrolyzed hemicelluloses was recovered by mixing a batch of 2 g steam-treated dried particles with 30 cm^3 distilled water. The resulting slurry was agitated overnight to recover the water soluble fraction. An aliquot of the water soluble fraction was also collected to analyze the sugar yield during washing. The water insoluble (WI) fractions were then washed with approximately 50 cm^3 water centrifuged at a relative centrifugal force (RCF) of 4000 × g for 10 min for four times to minimize WS fraction in the insoluble fraction. Acid post-pretreatment hydrolysis on the extracted sugars in the resulted 200 cm^3 water from the water insoluble fractions was carried out in a final sulfuric acid concentration of 30 $kg\ m^{-3}$ at 121 °C for 60 min. This ensures all oligomers were converted into monomers for HPLC quantification. Furfural and HMF (5-hydroxylmethylfurfural) in water soluble fraction were measured on Dionex (Sunnyvale, CA) HPLC (ICS-3000) equipped with an AS 50 auto sampler, ED50 electrochemical detector, GP 50 gradient pump and anion exchange column (Biorad Aminex HPX-87H). For simplifying the interpretation of the results, we followed the previous research [24]. Recovered hemicelluloses sugars were restricted to mannose, galactose, xylose, and arabinose. Recovered glucose represented the sugar monomer recovered from both hemicelluloses and cellulose.

The washed water insoluble fractions were analyzed for acid insoluble lignin and carbohydrates using TAPPI-T-222 om-88 (TAPPI, 1994) method [25]. The hydrolyzate from this analysis was retained and analyzed for soluble lignin by reading the absorbance at 205 nm [26]. Sugars, furfural and HMF from solid phase materials and water soluble fractions were measured on Dionex HPLC. All HPLC analysis was done in duplicate.

2.8. Morphology analysis

SEM observations of the samples' ultrastructure were carried out on oven-dry powder samples, which were mounted on specimen stubs and coated with gold under vacuum. All photographs were taken at 10–20 kV accelerating voltage by using a scanning electron microscope Hitachi N-3000 (Hitachi, City, Japan) with an energy dispersive X-ray spectrometer (EDAX EDS).

3. Results and discussion

3.1. Fuel properties

Fig. 2 shows the untreated and steam treated pellets from this study [2]. The moisture content of the pellets was between 5.3 and 6.0% (wet basis) and the high heating value of pellets was between 18.82 MJ kg^{-1} and 20.09 MJ kg^{-1} (Table 1). The steam treated pellets showed a higher mechanical strength and moisture sorption resistance than untreated pellets [2,27,28]. The color of the pellets turned from white to dark brown color with the steam treatment severity. These color change was due to Maillard reactions of mono-saccharides and extractives degradation after steam treatment [27]. The color coordinates measured on the treated and untreated pellets using a Hunterscan scale (L*, a*, b*) were highly correlated with the elemental and chemical compositions (lignin and extractive) of the pellet.

3.2. Compaction

Fig. 3 shows the force displacement graph of the untreated and steam-treated bulk Douglas fir particles under compression. For the untreated sample, the axial force acted on the particles increased slightly from 0 N to less than 500 N when

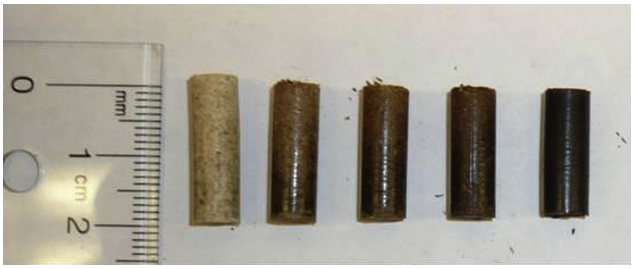

Fig. 2 – Pellets made from untreated and steam-treated Douglas fir. From left to right shows pellets made from compacting bulk particles (a) untreated, (b) 200 °C – 5 min, (c) 200 °C – 10 min, (d) 220 °C – 5 min (e) 220 °C – 10 min.

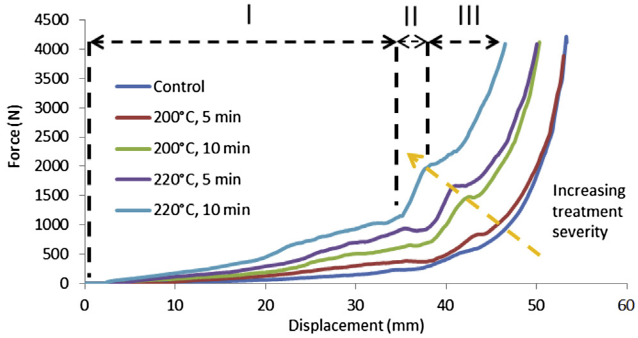

Fig. 3 – Compaction of untreated and steam-treated Douglas fir particles at four steam treatment severities. Region I represent initial volume reduction during which particles undergo rearrangement followed by initial packing. Region II that corresponds to a sharp increase in force is due to increased activity of lignin in steam treated pellets. Region III is the final stage of compaction where cellulose fraction is compacted.

piston traveled from 0 to 40 mm. It is expected that as the volume decreases rearrangement of the particles takes place during this phase of compaction. The force increased more rapidly as the piston continued downward. The particles pressed against each other to form a slug of pellet. Densification took place when the displacement was between 37 and 55 mm (i.e. roughly equal to the length of the resulted untreated pellet of 18.34 mm from Table 2). It is postulated that within this pressure region, the particles underwent a plastic deformation forming a cohesive bonding between particles. There must have also been a degree of mechanical interlocking of fibers. It is also thought that particles experienced a plastic (non-elastic) deformation during the final stages of compaction.

For steam-treated particles, depending on the steam treatment severity, their force–deformation diagram deviated from that for the untreated particles (Fig. 3). The compression behavior of steam-treated samples could be divided into three regions. The first region (Region I) appears to corresponding to the particle packing region where the rearrangement of large and small particles takes place. The second region (Region II) represents a rather sharp increase in force vs. displacement. This region could represent the initial compressing phase of particles where the new structure of condensed lignin or pseudolignin undergoes plasticization [6]. The untreated sample did not exhibit the region II. As treatment severity increased, Region II became more pronounced. The third region (Region III) represents the second compression phase where the non-modified chemical components, e.g. cellulose underwent deformation and interlocking. The existence of three compression regions became more distinct for the samples treated with increasing treatment severity.

The initial slope of the axial compression force and displacement increases with steam treatment severity. The initial slope in region I represents the elastic modulus of the bulk powder between 1082 and 2486 MPa (Table 3). Among the three major components (lignin, cellulose, hemicelluloses), cellulose has a crystalline structure with the highest modulus of elasticity. Hemicelluloses are the visco-elastic components of wood fiber which introduce viscous effect among the amorphous lignin and the crystalline structure of cellulose (rigid) in the fiber [29]. The hydrolysis of hemicelluloses due to steam treatment leads to an increase in brittleness of the samples.

Table 3 lists the increase in calculated elastic modulus from 93 MPa for untreated particles to 290 MPa for steam-treated Douglas fir at 220 °C – 5 min (Table 1). The pellets made with steam treatment at 220 °C had the highest variability of the elastic modulus. We postulate that polymeric components like lignin and sugars degrade at this high treatment temperature, and the degree of the reaction is non-homogenous due to the heterogeneous structure of the biomass. Particles produced from different parts of a wood log contain different chemical constituents. The elastic modulus is related to the chemical composition of the treated materials, and therefore the most severe steam treatment would cause a relatively large variation in mechanical properties of pellets. A less severe treatment at 200 °C would be the optimum temperature to produce the hardest pellets in this study with a lesser variation in mechanical properties.

Table 1 – Fuel properties of pellets made from untreated and steam treated D. Fir.

Treatment		Water mass fraction[a] (%)	High heating value[a] (MJ kg^{-1})	Ash mass fraction[b] (g kg^{-1})	C (g kg^{-1})	H (g kg^{-1})
Untreated	Avg.	6.9	18.82	0.27	48.44	6.23
	Std dev.	0.1	0.3	0.02		
200 °C – 5 min	Avg.	6.0	18.94	0.32	49.14	6.08
	Std dev.	0.6	0.04	0.01		
200 °C – 10 min	Avg.	6.0	19.15	0.32	50.46	6.10
	Std dev.	0.3	0.04	0.01		
220 °C – 5 min	Avg.	6.0	19.5	0.52	52.42	5.95
	Std dev.	0.2	0.05	0.09		
220 °C – 10 min	Avg.	5.3	20.09	0.41	53.09	5.91
	Std dev.	0.1	0.01	0.02		

Note: the reported mass fraction (g kg^{-1}) is based on the totally dried material.

a Number of measurements, $N = 2$.

b Number of measurements, $N = 3$.

Table 2 – Physical properties of grind particles and dimensions of pellets.

Trial		Feedstock		Pellet			
		Moisture content[a] (%)	Geometric mean diameter[a] (mm)	Mass[b] (g)	Length[b] (mm)	Diameter[b] (mm)	Pellet density (kg m^{-3})
Measured immediately after production							
Untreated	Average	8.70	0.42	0.69	18.34	6.61	1090
	SD	3.00	0.03	0.02	0.36	0.03	40
200 °C, 5 min	Average	9.40	0.45	0.68	17.60	6.61	1120
	SD	0.20	0.01	0.03	0.15	0.02	50
200 °C, 10 min	Average	10.00	0.40	0.79	20.96	6.64	1090
	SD	0.20	0.02	0.01	0.42	0.02	10
220 °C, 5 min	Average	11.80	0.38	0.79	21.19	6.62	1080
	SD	0.50	0.02	0.01	0.69	0.02	40
220 °C, 10 min	Average	8.60	0.35	0.79	21.63	6.61	1070
	SD	0.10	0.04	0.01	0.66	0.01	30
Measured after one week of production							
Untreated	Average	–	–	0.68	18.41	6.63	1070
	SD	–	–	0.01	0.44	0.02	20
200 °C, 5 min	Average	–	–	0.67	17.54	6.62	1110
	SD	–	–	0.10	0.16	0.02	10
200 °C, 10 min	Average	–	–	0.79	20.90	6.63	1090
	SD	–	–	0.01	0.40	0.02	10
220 °C, 5 min	Average	–	–	0.78	21.31	6.60	1080
	SD	–	–	0.02	0.67	0.02	40
220 °C, 10 min	Average	–	–	0.78	21.70	6.59	1060
	SD	–	–	0.01	0.78	0.01	30

a Number of measurements, $N = 3$, for all physical parameters of feedstock.
b Number of measurements, $N = 15$, for all physical parameters of pellets.

3.3. *Stress relaxation*

Fig. 4 plots the stress relaxation behavior of compressed bulk treated and untreated particles. The maximum compressive stress was 131 MPa (equivalent to 4000 N on a 6.2 mm diameter pellet). The residual stress of the untreated pellet decreased from 131 (100%) to 113 MPa (86%) when t was 5 s. The residual stress of steam treated pellet treated at 200 °C at relaxation time of 5 s was 82.2%. For pellets made from steam-treated particles at 220 °C for 5 and 10 min, the residual stress at relaxation time of 5 s were 78.6% and 77.8%, respectively. The final residual stress of untreated and steam-treated samples at the relaxation time of 30 s was 75.6, 71.2, 70.8, 67.8, 67.3% of the initial stress. The steam treatment time has a relatively lesser effect on the stress relaxation behavior of the pellets than the temperature. The lower the final residual stress of the sample is, the less expansion of the final pellet is. This observation agrees well with the pellet dimensions measured immediately after removal of the pellet from the die and after one week, respectively (Table 2). The physical dimensional changes of pellet mainly occur in the length direction. Only the pellets made from untreated biomass expanded from 18.34 to 18.41 mm in length and from 6.61 to 6.63 mm in radial direction. The pellets made from steam-treated samples did not change much in both the length and the radial direction, exhibiting a consistent dimensional stability. The increase in

Table 3 – Mechanical parameters from compression and hardness tests of untreated and steam treated D. Fir.

Treatment	Compression test					Hardness test					
	Elastic modulus[a] (MPa)			Asymptotic modulus[a] (MPa)		Hardness modulus[b] (GPa)		Meyer hardness[b] (N mm^{-2})		Maximum breaking force[b] (N)	
	Average	SD	R^2	Average	SD	Average	SD	Average	SD	Average	SD
Untreated	741.16	92.77	0.93	1331.34	29.69	11.41	9.60	1.6	0.2	18.0	4.0
200 °C – 5 min	1082.91	107.88	0.97	1250.63	15.81	17.16	6.71	2.1	0.3	25.7	2.1
200 °C – 10 min	1657.31	176.34	0.98	1244.44	17.97	16.96	6.02	2.3	0.9	34.5	11.9
220 °C – 5 min	2249.82	289.64	0.98	1193.02	13.46	19.56	4.83	6.6	2.1	59.3	11.1
220 °C – 10 min	2486.36	267.47	0.98	1173.55	7.27	15.82	2.01	5.6	1.8	44.2	7.6

a Number of measurements, $N = 15$.
b Number of measurements, $N = 5$.

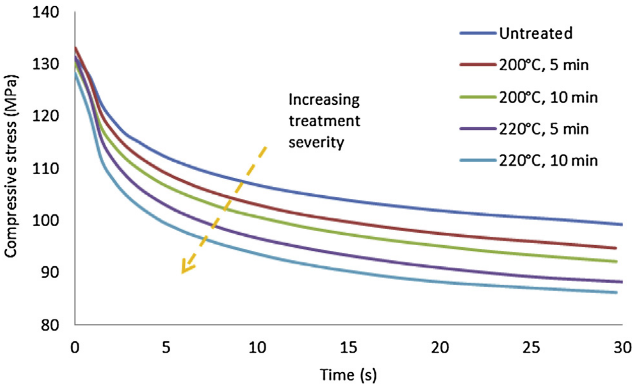

Fig. 4 – Stress relaxations of untreated and steam-treated Douglas fir particles in bulk after initial compression to 4000 N at four steam treatment severities.

length of the pellets after one week is due to stress relaxation. Cellulose, hemicellulose and lignin, each as polymer tends to relax the residual stresses by expansion as time progresses [13–15]. It appears steam treatment depolymerizes hemicelluloses to a degree that its visco-elastic effect within the cellulose and lignin matrix is minimized. A faster relaxation of the steam-treated pellet indicated that a shorter holding time is required for the steam-treated material to produce good quality pellet. This indicates the capacity of a press mill in increasing the production rate of steam-treated material without decreasing the pellet quality compared to the traditional wood pellet production is possible. A recent published research [30] found that the pellet production rate of torrefied spruce increased with the die temperature but correlated negatively with the bulk density. Peng [31] raised the die temperature to about 200 °C in order to produce durable pellets from torrefied biomass. Our choice of 70 °C for the die temperature experiments seems to be at the lower end of the pellet temperature in commercial pelletization operation. In future research, we will increase the die temperature to higher levels in order to determine the changes in mechanical (rheological) properties of manufactured pellets.

From Table 3, the asymptotic modulus of the untreated pellet was 1331 MPa which was the highest among all samples. The asymptotic modulus of samples after steam treatment decreased with increasing the severity from 1251 to 1174 MPa. This showed that the rigidity of the sample decreased with increasing the severity of steam treatment. The changes in wood rigidity after steam treatment are most likely related to modifications in the chain mobility of the cell wall polymers by the hydrolysis of hemicellulose and the condensations of lignin Refs. [29,32]. From Table 4, the concentration of polysaccharides (arabinan, galactan, glucan, xylan and mannan) in the solid residue decreased with increasing steam treatment severity. The autohydrolysis of softwood takes place in the presence of saturated steam at temperatures between 180 and 240 °C, which cleaves the acetyl groups of acetylated hemicelluloses to generate the acetic acid for facilitating the hydrolysis of the polysaccharides from cell wall to generate the

Table 4 – Lignin and sugars of the solid residue and liquid fraction of untreated and steam treated D. Fir.

Treatment	Extractives (%)[a]	Acid insoluble lignin[a] (g kg^{-1})	Acid soluble lignin[a] (g kg^{-1})	Arabinan	Galactan	Glucan	Xylan	Mannan	Total sugars
		Solid residue[1] (g kg^{-1} of total sugars)							
Untreated	1.42	26.00	0.34	0.92	2.65	54.61	4.42	10.02	98.96
200 °C – 5 min	2.22	28.30	0.31	0.28	1.68	58.86	4.28	9.61	103.32
200 °C – 10 min	3.23	31.70	0.43	0.21	1.09	58.90	3.26	7.32	102.91
220 °C – 5 min	8.84	32.20	0.32	0.12	1.03	60.31	3.46	7.11	104.55
220 °C – 10 min	7.36	35.70	0.47	0.07	0.30	57.34	2.14	3.94	99.96
Water Soluble Fraction[1] (g kg^{-1} of dry wood)									
		Furfural[b,c]	HMF[b]	Arabinose	Galactose	Glucose	Xylose	Mannose	Total sugars
200 °C – 5 min		–	2.70	0.18 (6%)	0.56 (20%)	0.44 (16%)	0.47 (17%)	1.36 (48%)	2.83
200 °C – 10 min		–	3.59	0.07 (2%)	0.22 (6%)	0.82 (23%)	0.47 (13%)	2.02 (56%)	3.60
220 °C – 5 min		–	5.79	0.17 (3%)	0.51 (9%)	0.99 (17%)	0.82 (14%)	3.31 (57%)	5.80
220 °C – 10 min		–	7.12	0.02 (1%)	0.07 (3%)	0.52 (26%)	0.16 (8%)	1.26 (62%)	2.03

a Number of measurements, $n = 2$, parentheses shows the percentage of individual mono-sugar recovery in water fraction.
b Units are in g m^{-3}.
c Furfural were below detection limit of HPLC (<2 g m^{-3}).

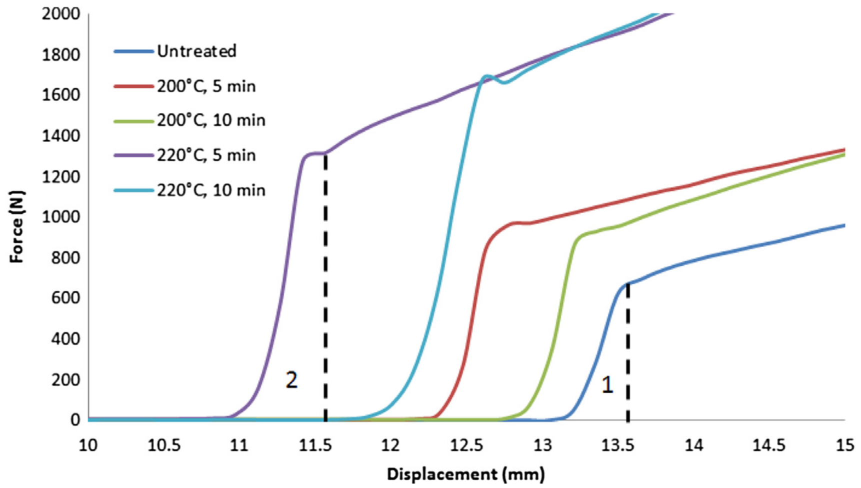

Fig. 5 – Force displacement graph of untreated and steam-treated Douglas fir pellets at different severities during extrusion. Area 1 and 2 corresponds to the extrusion energy of untreated pellet and steam-treated Douglas fir pellet at 200 °C – 5 min.

water soluble mono-saccharides (arabinose, galactose, glucose, xylose and mannose) [6,33]. The mono-sugars released by acid hydrolysis were glucose (0.44–0.99 g kg^{-1}), xylose (0.47–0.82 g kg^{-1}) and galactose (0.07–0.56 g kg^{-1}). Glucose was formed from the hydrolysis of galactoglucomannan (hemicelluloses) and glucan (cellulose). The overall sugar analysis is consistent with the fact that galactoglucomannan are the main hemicelluloses in softwood, whereas xylans are the second most abundant. Evidently the total soluble sugars and pseudolignin affected the compaction and extrusion behavior during pelletization. Future work will focus on investigating which individual sugar or lignin would improve the binding characteristics of wood fibers.

3.4. *Pellet extrusion*

Fig. 5 shows the force vs. displacement graph when the piston moved to push the pellet out from the die. The area under the curve represents the pellet expulsion energy [9]. For untreated pellet, the force increased from 0 N to roughly 480 N in order to initiate the pellet movement. This indicates that at least 480 N is required to overcome the static friction between the inner wall of the die and the pellet. For steam-treated pellets, the maximum frictional force required to be overcome to initiate a pellet movement increased with treatment severity by about 2–3 times of frictional force for the untreated pellet (Table 5). Similar trend was also observed for the expulsion energy. We observed that the steam-treated pellet was sticky upon exit from the die. We speculate the increase in particle surface roughness (Fig. 6b) and the increase in mono-saccharides and extractives (Table 4) contribute to the increase in required energy for extruding the pellet made with increasing steam treatment severity.

3.5. *Hardness test*

A good correlation between pellet durability determined by European wood pellet standards (EN 15210-1) and compression strength by using 25 pellets was reported previously [34]. Table 3 lists the hardness modulus, Meyer hardness and the maximum breaking force of the pellets made from untreated and steam-treated Douglas fir at different severity. The hardness modulus of untreated pellet is 11.41 GPa. This value is close to the reported value of 13.6 GPa for the costal Douglas fir with a water mass fraction of 12% [35]. The hardness modulus of steam-treated pellets increase from 17.16 to a maximum of 19.56 GPa at the treatment condition of 220 °C – 5 min, and decreased to 15.82 GPa for the steam-treated

Table 5 – Energy input for pelletization (compression and extrusion).

Treatment	Compaction				Extrusion			
	Maximum compaction force[a] (N)		Specific compaction energy[a] (J cm^{3} g^{-1})		Maximum frictional force[b] (N)		Specific energy[b] (mJ g^{-1})	
	Average	SD	Average	SD	Average	SD	Average	SD
Untreated	4290	70	20.45	1.67	476.20	92.43	48.86	3.31
200 °C – 5 min	4190	145	22.27	1.39	832.50	71.43	117.67	29.85
200 °C – 10 min	4120	39	29.28	1.71	977.59	219.94	117.25	13.84
220 °C – 5 min	4297	54	36.25	4.78	1091.60	207.72	177.53	45.40
220 °C – 10 min	4079	27	38.15	2.14	1301.99	137.74	250.32	25.94

a Numerical integration by trapezoidal rule under the stress strain curve of each sample, (N = 15).
b Numerical integration by trapezoidal rule under the stress strain curve for each sample, (N = 3).

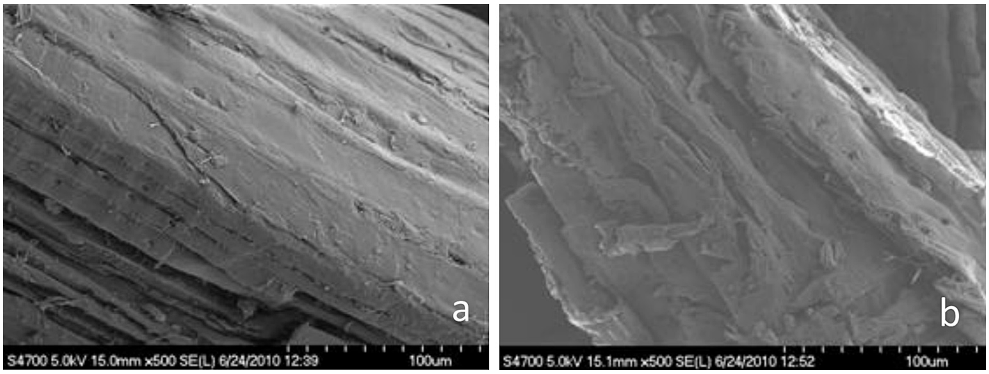
a
S4700 5.0kV 15.0mm x500 SE(L) 6/24/2010 12:39
100um
b
S4700 5.0kV 15.1mm x500 SE(L) 6/24/2010 12:52
100um

Fig. 6 – SEM pictures of (a) untreated ground particle by hammer mill with 1.6 mm screen opening and (b) steam-treated particles at 4.53 severity with ×500 magnification.

pellets treated at 220 °C – 10 min. For 200 °C, there is no significant difference between the elastic modulus of treated samples with p-value > 0.05. The depolymerization of hemicelluloses results in an increase in crystallinity of cellulose from 49.5 to 67.5% measured by X-ray diffraction reported in our previous publication [2], and thereby increasing the brittleness of the pellet. However, when the steam treatment severity increased to 220 °C – 10 min, partial cellulose was degraded as indicated by a decrease in glucan from 60.31 to 57.34% (Table 4). Both Meyer hardness and maximum breaking force followed the same trend as the hardness modulus due to the chemical compositional changes brought about by hemicelluloses hydrolysis and cellulose degradation. These measurements of the Meyer hardness and the hardness modulus provided a means of evaluating the strength of pellets to withstand compressive forces during storage and transportation. In this research, the maximum breaking force, Meyer hardness and the hardness modulus increased with treatment temperature and time to 220 °C – 5 min and reached a maximum and followed by a decrease for the pellets treated at 220 °C–10 min (Table 3). This follows the same trend as the recovery of the total mono-sugars in water soluble fraction (Table 4). The decrease in sugars was due to the degradation by dehydration and formation of furans derivatives (e.g. furfural, 5-hydroxylmethylfufural) [33]. They can form strong condensation bonding with the low molecular weight lignin to yield so called pseudolignin [6,36,37]. Our previous work has attempted to model the pseudolignin formation during steam explosion [6]. We will take the role of pseudolignins into account for the improvement of wood pellet strength as future work.

Apart from pseudolignin, we speculate that the mono-sugars also play an important role in binding during pelletization as depicted by the cross section SEM photos of untreated and treated pellets (Fig. 6). For untreated pellet (Fig. 6a), there are clear boundaries between individual particles and forms layers. Poor adhesion is due to a lack of strong binding force between inter-particles to minimize expansion by stress relaxation. In contrast, the individual particles pack closely to each other and the dark region exists between boundaries between individual particles of steam-treated pellet (Fig. 6b). The dark region corresponds to non-conducting material under the scanning electron microscope, which could be corresponding to the presence of mono-sugars. Mono-sugars forms gelation structure with strong chemical bonding between individual particles upon cooling right after extrusion from the die. Recent research showed that a single pretreatment can facilitate both pelletization and subsequent enzymatic hydrolysis without the need for a further pretreatment step for ethanol production [38]. This may indicate the steam exploded pellets in this study could be an excellent feedstock for ethanol production. We will use Raman confocal microscope to investigate the chemical bonding in future work.

The improvement in mechanical strength and moisture adsorption resistance of steam-treated pellets are attractive for outdoor storage for end-users. However, these mono-sugars are questions to be easily leached out by rain or melted snow during outdoor storage, and thereby deteriorating the durability of pellets. Future research can focus on evaluating the effect of weather on the durability of steam-treated pellets. While the authors believe that this work exemplifies the difference between treatments - there is a reasonable concern that there may be substrate factors that influence the transfer of the results obtained, to other sources other than Douglas fir.

4. Conclusions

The rheological properties of pelletization of steam-treated Douglas fir at four different severities using a single die were investigated. Hydrolysis of hemicelluloses and condensations of lignin contribute to the increase in elasticity and the decrease in rigidity of pellets. The increase in particle surface roughness along with increased concentration of mono-sugars and extractives contribute to the increase in required energy for pushing the treated pellets from the die. The improvement in hardness and dimensional stability of steam treated pellets can be explained by the binding role of mono-sugars released from Douglas fir during hydrothermal treatment.

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Appendix

The relaxation data for each sample were analyzed by the method described in [14,20]. Equation (A.1) is derived from the rheological equation of the generalized Maxwell model [39]. The force vs. time for the relaxation curve was normalized and linearized and represented as a straight line by,

$$\frac{\sigma_0 t}{\sigma_0 - \sigma(t)} = k_1 + k_2 t \tag{A.1}$$

The asymptotic modulus (E_A) is defined as the resistance of the materials to further deform at infinite time, therefore,

$$\sigma(t) = E_A \varepsilon \tag{A.2}$$

where E_A is the asymptotic modulus (MPa) and ε is the strain (dimensionless or m m^{-1}).

Rearranging equation (A.1),

$$\frac{\sigma_0 t}{\sigma_0 - \sigma(t)} = k_1 + k_2 t$$

$$\frac{\sigma_0}{\sigma_0 - \sigma(t)} = \frac{1}{t} k_1 + k_2$$

Substitute equation (A.2) into equation (A.1), we have

$$\frac{\sigma_0}{\sigma_0 - E_A \varepsilon} = \frac{1}{t} k_1 + k_2$$

As the pellet undergoes stress relaxation for a long time, we can say if time is close to infinity, we have

$$t \to \infty$$

$$\frac{\sigma_0}{\sigma_0 - E_A \varepsilon} = \underbrace{\frac{1}{2} k_1}_{0} + k_2$$

$$\frac{\sigma_0}{\sigma_0 - E_A \varepsilon} = k_2$$

$$k_2 \sigma_0 - \sigma_0 = k_2 E_A \varepsilon$$

Rearranging,

$$E_A = \frac{\sigma_0}{\varepsilon} \left(\frac{k_2 - 1}{k_2} \right)$$

Therefore,

$$E_A = \frac{\sigma_0}{\varepsilon} \left(1 - \frac{1}{k_2} \right) \tag{A.3}$$

where E_A is the asymptotic modulus (MPa) and ε is the strain (dimensionless or m m^{-1}).

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